

## CLAIMS

What is claimed is:

1           Claim 1. A process for preparing diblock and triblock  
2 copolymers comprising the steps of:

3           (a) performing radical polymerization of N-vinyl-2-  
4 pyrrolidone in the presence of a radical initiator, a chain  
5 transfer agent and an alcoholic solvent to form hydroxy-  
6 terminated poly (N-vinylpyrrolidone) and

7           (b) performing ionic polymerization of monomers or  
8 comonomers in the presence of a catalyst and a macroinitiator  
9 wherein said macroinitiator is the hydroxy-terminated poly  
10 (N-vinylpyrrolidone) formed in step (a) thereby preparing said  
11 diblock and triblock copolymers.

1           Claim 2. The process in accordance with claim 1 wherein  
2 said monomers or comonomers are cyclic or vinylic.

1           Claim 3. The process in accordance with claim 2 wherein  
2 said monomers are cyclic and are selected from the group  
3 consisting of 3,6-dimethyl-1,4-dioxane-2,5-dione,  $\epsilon$ -  
4 caprolactone and  $\gamma$ -caprolactone.

1           Claim 4. The process in accordance with claim 1 wherein  
2   said monomers or comonomers are polyester.

1           Claim 5. The process in accordance with claim 4 wherein  
2   said polyester is degradable.

1           Claim 6. The process in accordance with claim 5 wherein  
2   said polyester is selected from the group consisting of  
3   poly(D,L-lactide), poly(D-lactide), poly (L-lactide),  
4   poly( $\epsilon$ -caprolactone) and poly ( $\gamma$ -caprolactone).

1           Claim 7. The process in accordance with claim 1 wherein  
2   said alcoholic solvent is selected from the group consisting  
3   of methanol, ethanol, isopropyl alcohol, n-propanol, n-  
4   butanol, 2-butanol, *tert*-butanol, 1-pentanol and 2-pentanol.

1           Claim 8. The process in accordance with claim 1 wherein  
2   said chain transfer agent is a thiol derivative selected from  
3   the group consisting of 2-mercaptoethanol, 3-mercapto-1-  
4   propanol, 3-mercapto-2-propanol, 4-mercapto-1-butanol, 3-  
5   mercapto-2-butanol and 6-mercapto-1-hexanol.

1           Claim 9. The process in accordance with claim 1 wherein  
2   said radical initiator is an azo derivative selected from the  
3   group consisting of 2,2'-azobis(2-methyl-N-(2-hydroxyethyl)-  
4   propionamide); 2,2'-azobis(2-methyl-N-[2-(1-hydroxybutyl)]  
5   propionamide and 1,1'-azobis(cyclohexane-carbonitrile).

1           Claim 10. The process in accordance with claim 1 wherein  
2   said catalyst is aluminum or tin alkoxides.

1           Claim 11. The process in accordance with claim 1 wherein  
2   said poly(N-vinylpyrrolidone) formed in step (a) comprises a  
3   hydroxyl group on at least one chain end.

1           Claim 12. The process in accordance with claim 1 wherein  
2   said poly (N-vinylpyrrolidone) formed in step (a) is isolated  
3   by dissolution and precipitation.

1           Claim 13. The process in accordance with claim 12  
2   wherein the solvent for said dissolution is selected from  
3   the group consisting of methanol, ethanol,  
4   isopropanolisopropyl alcohol, acetone, 2-butanone, 4-methyl-  
5   2-pentanone, dichloromethane and tetrahydrofuran.

1           Claim 14. The process in accordance with claim 13  
2    wherein at least two solvents are combined for said  
3    dissolution.

1           Claim 15. The process in accordance with claim 12  
2    wherein the solvent for said precipitation is selected from  
3    the group consisting of diethyl ether, *tert*-butyl methyl  
4    ether, hexane derivatives, heptane derivatives, ethyl  
5    acetate, isopropyl acetate, toluene and xylene derivatives.

1           Claim 16. The process in accordance with claim 15  
2    wherein at least two solvents are combined for said  
3    precipitation.

1           Claim 17. The process in accordance with claim 1 wherein  
2    said poly (N-vinylpyrrolidone) formed in step (a) is dried  
3    under vacuum at a final temperature over 100°C.

1           Claim 18. The process in accordance with claim 1 wherein  
2    said poly (N-vinylpyrrolidone) formed in step (a) is dried by  
3    azeotropic distillation using an inert organic solvent.

1           Claim 19. The process in accordance with claim 18  
2   wherein said inert organic solvent is selected from the group  
3   consisting of toluene, xylene derivatives and heptane  
4   derivatives.

1           Claim 20. The process in accordance with claim 1 wherein  
2   said diblock and triblock copolymers are isolated by  
3   precipitation using an inert organic solvent.

1           Claim 21. The process in accordance with claim 20  
2   wherein said inert organic solvent is selected from the group  
3   consisting of diethyl ether, *tert*-butyl methyl ether, hexane  
4   derivatives, heptane derivatives, ethyl acetate, isopropyl  
5   acetate, toluene and xylene derivatives.

1           Claim 22. The process in accordance with claim 21  
2   wherein at least two inert organic solvents are combined for  
3   said precipitation.

1           Claim 23. The process in accordance with claim 1 wherein  
2   said diblock and triblock copolymers are purified by charcoal  
3   treatment.

1           Claim 24. The process in accordance with claim 1 wherein  
2    said poly(N-vinylpyrrolidone) formed in step (a) has a  
3    molecular weight between 1,000 D and 700 kD.

1           Claim 25. The process in accordance with claim 1 wherein  
2    said diblock and triblock copolymers have a molecular weight  
3    between 2,000 D and 700 kD.

1           Claim 26. The process in accordance with claim 1 wherein  
2    said diblock and triblock copolymers self-assemble in  
3    polymeric micelles in aqueous solution.

1           Claim 27. The process in accordance with claim 1 wherein  
2    said diblock and triblock copolymers self-assemble in  
3    stabilized nanoparticles in aqueous solution.

1           Claim 28. The diblock copolymer prepared by the process  
2    of claim 1.

1           Claim 29. The diblock copolymer of claim 28 wherein said  
2    diblock copolymer is poly(N-vinylpyrrolidone)-*block*-poly (D,  
3    L -lactide).

1           Claim 30. The triblock copolymer prepared by the process  
2   of claim 1.

1           Claim 31. The triblock copolymer of claim 30 wherein  
2   said triblock copolymer is poly(D,L-lactide)-*block*-poly (N-  
3   vinylpyrrolidone)-*block*-poly (D, L-lactide).

1           Claim 32. A process for preparing diblock and triblock  
2   copolymers comprising the steps of:

3           (a)performing radical polymerization of N-vinyl-2-  
4   pyrrolidone in the presence of a radical initiator, a chain  
5   transfer agent and an alcoholic solvent to form hydroxy-  
6   terminated poly (N-vinylpyrrolidone) and

7           (b) performing ionic polymerization of monomers or  
8   comonomers in the presence of a base and a macroinitiator  
9   wherein said macroinitiator is the hydroxy-terminated poly  
10   (N-vinylpyrrolidone) formed in step (a)thereby preparing said  
11   diblock and triblock copolymers.

1           Claim 33. The process in accordance with claim 32  
2   wherein said monomers or comonomers are cyclic or vinylic.

1           Claim 34. The process in accordance with claim 33  
2   wherein said monomers are cyclic and are selected from the  
3   group consisting of 3,6-dimethyl-1,4-dioxane-2,5-dione,  $\epsilon$ -  
4   caprolactone and  $\gamma$ -caprolactone.

1           Claim 35. The process in accordance with claim 32  
2   wherein said monomers or comonomers are polyester.

1           Claim 36. The process in accordance with claim 35  
2   wherein said polyester is degradable.

1           Claim 37. The process in accordance with claim 36  
2   wherein said polyester is selected from the group consisting  
3   of poly(D,L-lactide), poly(D-lactide), poly (L-lactide),  
4   poly( $\epsilon$ -caprolactone) and poly ( $\gamma$ -caprolactone).

1           Claim 38. The process in accordance with claim 32  
2   wherein said alcoholic solvent is selected from the group  
3   consisting of methanol, ethanol, isopropyl alcohol, n-  
4   propanol, n-butanol, 2-butanol, *tert*-butanol, 1-pentanol and  
5   2-pentanol.



1           Claim 39. The process in accordance with claim 32  
2   wherein said chain transfer agent is a thiol derivative  
3   selected from the group consisting of 2-mercaptoethanol, 3-  
4   mercapto-1-propanol, 3-mercapto-2-propanol, 4-mercapto-1-  
5   butanol, 3-mercapto-2-butanol and 6-mercapto-1-hexanol.

1           Claim 40. The process in accordance with claim 32  
2   wherein said radical initiator is an azo derivative selected  
3   from the group consisting of 2,2'-azobis(2-methyl-N-(2-  
4   hydroxyethyl)-propionamide); 2,2'-azobis(2-methyl-N-[2-(1-  
5   hydroxybutyl)] propionamide and 1,1'-azobis(cyclohexane-  
6   carbonitrile).

1           Claim 41. The process in accordance with claim 1 wherein  
2   said base is potassium or sodium hydride.

1           Claim 42. The process in accordance with claim 32  
2   wherein said poly(N-vinylpyrrolidone) formed in step (a)  
3   comprises a hydroxyl group on at least one chain end.

1           Claim 43. The process in accordance with claim 32  
2   wherein said poly (N-vinylpyrrolidone) formed in step (a) is  
3   isolated by dissolution and precipitation.

1           Claim 44. The process in accordance with claim 43  
2    wherein the solvent for said dissolution is selected from  
3    the group consisting of methanol, ethanol,  
4    isopropanolisopropyl alcohol, acetone, 2-butanone, 4-methyl-  
5    2-pentanone, dichloromethane and tetrahydrofuran.

1           Claim 45. The process in accordance with claim 44  
2    wherein at least two solvents are combined for said  
3    dissolution.

1           Claim 46. The process in accordance with claim 43  
2    wherein the solvent for said precipitation is selected from  
3    the group consisting of diethyl ether, *tert*-butyl methyl  
4    ether, hexane derivatives, heptane derivatives, ethyl  
5    acetate, isopropyl acetate, toluene and xylene derivatives.

1           Claim 47. The process in accordance with claim 46  
2    wherein at least two solvents are combined for said  
3    precipitation.

1           Claim 48. The process in accordance with claim 32  
2    wherein said poly (N-vinylpyrrolidone) formed in step (a) is  
3    dried under vacuum at a final temperature over 100°C.

1           Claim 49. The process in accordance with claim 32  
2   wherein said poly (N-vinylpyrrolidone) formed in step (a) is  
3   dried by azeotropic distillation using an inert organic  
4   solvent.

1           Claim 50. The process in accordance with claim 49  
2   wherein said inert organic solvent is selected from the group  
3   consisting of toluene, xylene derivatives and heptane  
4   derivatives.

1           Claim 51. The process in accordance with claim 32  
2   wherein said diblock and triblock copolymers are isolated by  
3   precipitation using an inert organic solvent.

1           Claim 52. The process in accordance with claim 51  
2   wherein said inert organic solvent is selected from the group  
3   consisting of diethyl ether, *tert*-butyl methyl ether, hexane  
4   derivatives, heptane derivatives, ethyl acetate, isopropyl  
5   acetate, toluene and xylene derivatives.

1           Claim 53. The process in accordance with claim 52  
2   wherein at least two inert organic solvents are combined for  
3   said precipitation.

1           Claim 54. The process in accordance with claim 32  
2   wherein said diblock and triblock copolymers are purified by  
3   charcoal treatment.

1           Claim 55. The process in accordance with claim 32  
2   wherein said poly(N-vinylpyrrolidone) formed in step (a) has  
3   a molecular weight between 1,000 D and 700 kD.

1           Claim 56. The process in accordance with claim 32  
2   wherein said diblock and triblock copolymers have a molecular  
3   weight between 2,000 D and 700 kD.

1           Claim 57. The process in accordance with claim 32  
2   wherein said diblock and triblock copolymers self-assemble in  
3   polymeric micelles in aqueous solution.

1           Claim 58. The process in accordance with claim 32  
2   wherein said diblock and triblock copolymers self-assemble in  
3   stabilized nanoparticles in aqueous solution.

1           Claim 59. The diblock copolymer prepared by the process  
2   of claim 32.

1           Claim 60. The diblock copolymer of claim 59 wherein said  
2   diblock copolymer is poly(N-vinylpyrrolidone)-*block*-poly (D,  
3   L -lactide).

1           Claim 61. The triblock copolymer prepared by the process  
2   of claim 32.

1           Claim 62. The triblock copolymer of claim 61 wherein  
2   said triblock copolymer is poly(D,L-lactide)-*block*-poly (N-  
3   vinylpyrrolidone)-*block*-poly (D, L-lactide).

1           Claim 63. A process for preparing diblock and triblock  
2   copolymers comprising the steps of:

3           (a)performing radical polymerization of N-vinyl-2-  
4   pyrrolidone in the presence of a radical initiator and an  
5   alcoholic solvent to form hydroxy-terminated poly (N-  
6   vinylpyrrolidone) and

7           (b) performing ionic polymerization of monomers or  
8   comonomers in the presence of a catalyst and a macroinitiator  
9   wherein said macroinitiator is the hydroxy-terminated poly  
10   (N-vinylpyrrolidone) formed in step (a)thereby preparing said  
11   diblock and triblock copolymers.

1           Claim 64. The process in accordance with claim 63  
2   wherein said monomers or comonomers are cyclic or vinylic.

1           Claim 65. The process in accordance with claim 64  
2   wherein said monomers are cyclic and are selected from the  
3   group consisting of 3,6-dimethyl-1,4-dioxane-2,5-dione,  $\epsilon$ -  
4   caprolactone and  $\gamma$ -caprolactone.

1           Claim 66. The process in accordance with claim 63  
2   wherein said monomers or comonomers are polyester.

1           Claim 67. The process in accordance with claim 66  
2   wherein said polyester is degradable.

1           Claim 68. The process in accordance with claim 67  
2   wherein said polyester is selected from the group consisting  
3   of poly(D,L-lactide), poly(D-lactide), poly (L-lactide),  
4   poly( $\epsilon$ -caprolactone) and poly ( $\gamma$ -caprolactone).

1           Claim 69. The process in accordance with claim 63  
2   wherein said alcoholic solvent is selected from the group  
3   consisting of methanol, ethanol, isopropyl alcohol, n-  
4   propanol, -butanol, 2-butanol, *tert*-butanol, 1-pentanol and  
5   2-pentanol.

1           Claim 70. The process in accordance with claim 63  
2    wherein said radical initiator is an azo derivative selected  
3    from the group consisting of 2,2'-azobis(2-methyl-N-(2-  
4    hydroxyethyl)-propionamide); 2,2'-azobis(2-methyl-N-[2-(1-  
5    hydroxybutyl)] propionamide and 1,1'-azobis(cyclohexane-  
6    carbonitrile).

1           Claim 71. The process in accordance with claim 63  
2    wherein said catalyst is aluminum or tin alkoxides.

1           Claim 72. The process in accordance with claim 63  
2    wherein said poly(N-vinylpyrrolidone) formed in step (a)  
3    comprises a hydroxyl group on at least one chain end.

1           Claim 73. The process in accordance with claim 63  
2    wherein said poly (N-vinylpyrrolidone) formed in step (a) is  
3    isolated by dissolution and precipitation.

1           Claim 74. The process in accordance with claim 73  
2    wherein the solvent for said dissolution is selected from  
3    the group consisting of methanol, ethanol,  
4    isopropanolisopropyl alcohol, acetone, 2-butanone, 4-methyl-  
5    2-pentanone, dichloromethane and tetrahydrofuran.

1           Claim 75. The process in accordance with claim 74  
2   wherein at least two solvents are combined for said  
3   dissolution.

1           Claim 76. The process in accordance with claim 73  
2   wherein the solvent for said precipitation is selected from  
3   the group consisting of diethyl ether, *tert*-butyl methyl  
4   ether, hexane derivatives, heptane derivatives, ethyl  
5   acetate, isopropyl acetate, toluene and xylene derivatives.

1           Claim 77. The process in accordance with claim 76  
2   wherein at least two solvents are combined for said  
3   precipitation.

1           Claim 78. The process in accordance with claim 63  
2   wherein said poly (N-vinylpyrrolidone) formed in step (a) is  
3   dried under vacuum at a final temperature over 100°C.

1           Claim 79. The process in accordance with claim 63  
2   wherein said poly (N-vinylpyrrolidone) formed in step (a) is  
3   dried by azeotropic distillation using an inert organic  
4   solvent.



1           Claim 80. The process in accordance with claim 79  
2   wherein said inert organic solvent is selected from the group  
3   consisting of toluene, xylene derivatives and heptane  
4   derivatives.

1           Claim 81. The process in accordance with claim 63  
2   wherein said diblock and triblock copolymers are isolated by  
3   precipitation using an inert organic solvent.

1           Claim 82. The process in accordance with claim 81  
2   wherein said inert organic solvent is selected from the group  
3   consisting of diethyl ether, *tert*-butyl methyl ether, hexane  
4   derivatives, heptane derivatives, ethyl acetate, isopropyl  
5   acetate, toluene and xylene derivatives.

1           Claim 83. The process in accordance with claim 82  
2   wherein at least two inert organic solvents are combined for  
3   said precipitation.

1           Claim 84. The process in accordance with claim 63  
2   wherein said diblock and triblock copolymers are purified by  
3   charcoal treatment.

1           Claim 85. The process in accordance with claim 63  
2   wherein said poly(N-vinylpyrrolidone)formed in step (a) has a  
3   molecular weight between 1,000 D and 700 kD.

1           Claim 86. The process in accordance with claim 63  
2   wherein said diblock and triblock copolymers have a molecular  
3   weight between 2,000 D and 700 kD.

1           Claim 87. The process in accordance with claim 63  
2   wherein said diblock and triblock copolymers self-assemble in  
3   polymeric micelles in aqueous solution.

1           Claim 88. The process in accordance with claim 63  
2   wherein said diblock and triblock copolymers self-assemble in  
3   stabilized nanoparticles in aqueous solution.

1           Claim 89. The diblock copolymer prepared by the process  
2   of claim 63.

1           Claim 90. The diblock copolymer of claim 89 wherein said  
2   diblock copolymer is poly(N-vinylpyrrolidone)-*block*-poly (D,  
3   L -lactide).

1           Claim 91. The triblock copolymer prepared by the process  
2   of claim 63.

1           Claim 92. The triblock copolymer of claim 91 wherein  
2   said triblock copolymer is poly(D,L-lactide)-*block*-poly (N-  
3   vinylpyrrolidone)-*block*-poly (D, L-lactide).

1           Claim 93. A process for preparing diblock and triblock  
2   copolymers comprising the steps of:

3           (a)performing radical polymerization of N-vinyl-2-  
4   pyrrolidone in the presence of a radical initiator and an  
5   alcoholic solvent to form hydroxy-terminated poly (N-  
6   vinylpyrrolidone) and

7           (b) performing ionic polymerization of monomers or  
8   comonomers in the presence of a base and a macroinitiator  
9   wherein said macroinitiator is the hydroxy-terminated poly  
10   (N-vinylpyrrolidone) formed in step (a)thereby preparing said  
11   diblock and triblock copolymers.

1           Claim 94. The process in accordance with claim 93  
2   wherein said monomers or comonomers are cyclic or vinylic.

1           Claim 95. The process in accordance with claim 94  
2   wherein said monomers are cyclic and are selected from the  
3   group consisting of 3,6-dimethyl-1,4-dioxane-2,5-dione,  $\epsilon$ -  
4   caprolactone and  $\gamma$ -caprolactone.

1           Claim 96. The process in accordance with claim 93  
2   wherein said monomers or comonomers are polyester.

1           Claim 97. The process in accordance with claim 96  
2   wherein said polyester is degradable.

1           Claim 98. The process in accordance with claim 97  
2   wherein said polyester is selected from the group consisting  
3   of poly(D,L-lactide), poly(D-lactide), poly (L-lactide),  
4   poly( $\epsilon$ -caprolactone) and poly ( $\gamma$ -caprolactone).

1           Claim 100. The process in accordance with claim 93  
2   wherein said alcoholic solvent is selected from the group  
3   consisting of methanol, ethanol, isopropyl alcohol, n-  
4   propanol, n-butanol, 2-butanol, *tert*-butanol, 1-pentanol and  
5   2-pentanol.

1           Claim 101. The process in accordance with claim 93  
2   wherein said radical initiator is an azo derivative selected  
3   from the group consisting of 2,2'-azobis(2-methyl-N-(2-  
4   hydroxyethyl)-propionamide); 2,2'-azobis(2-methyl-N-[2-(1-  
5   hydroxybutyl)] propionamide and 1,1'-azobis(cyclohexane-  
6   carbonitrile).

1           Claim 102. The process in accordance with claim 93  
2   wherein said base is potassium or sodium hydride.

1           Claim 103. The process in accordance with claim 93  
2   wherein said poly(N-vinylpyrrolidone) formed in step (a)  
3   comprises a hydroxyl group on at least one chain end.

1           Claim 104. The process in accordance with claim 93  
2   wherein said poly (N-vinylpyrrolidone) formed in step (a) is  
3   isolated by dissolution and precipitation.

1           Claim 105. The process in accordance with claim 104  
2   wherein the solvent for said dissolution is selected from  
3   the group consisting of methanol, ethanol,  
4   isopropanolisopropyl alcohol, acetone, 2-butanone, 4-methyl-  
5   2-pentanone, dichloromethane and tetrahydrofuran.

1           Claim 106. The process in accordance with claim 105  
2   wherein at least two solvents are combined for said  
3   dissolution.

1           Claim 107. The process in accordance with claim 104  
2   wherein the solvent for said precipitation is selected from  
3   the group consisting of diethyl ether, *tert*-butyl methyl  
4   ether, hexane derivatives, heptane derivatives, ethyl  
5   acetate, isopropyl acetate, toluene and xylene derivatives.

1           Claim 108. The process in accordance with claim 107  
2   wherein at least two solvents are combined for said  
3   precipitation.

1           Claim 109. The process in accordance with claim 93  
2   wherein said poly (N-vinylpyrrolidone) formed in step (a) is  
3   dried under vacuum at a final temperature over 100°C.

1           Claim 110. The process in accordance with claim 93  
2   wherein said poly (N-vinylpyrrolidone) formed in step (a) is  
3   dried by azeotropic distillation using an inert organic  
4   solvent.

1           Claim 111. The process in accordance with claim 110  
2   wherein said inert organic solvent is selected from the group  
3   consisting of toluene, xylene derivatives and heptane  
4   derivatives.

1           Claim 112. The process in accordance with claim 93  
2   wherein said diblock and triblock copolymers are isolated by  
3   precipitation using an inert organic solvent.

1           Claim 113. The process in accordance with claim 112  
2   wherein said inert organic solvent is selected from the group  
3   consisting of diethyl ether, *tert*-butyl methyl ether, hexane  
4   derivatives, heptane derivatives, ethyl acetate, isopropyl  
5   acetate, toluene and xylene derivatives.

1           Claim 114. The process in accordance with claim 113  
2   wherein at least two inert organic solvents are combined for  
3   said precipitation.

1           Claim 115. The process in accordance with claim 93  
2   wherein said diblock and triblock copolymers are purified by  
3   charcoal treatment.

1           Claim 116. The process in accordance with claim 93  
2    wherein said poly(N-vinylpyrrolidone) formed in step (a) has  
3    a molecular weight between 1,000 D and 700 kD.

1           Claim 117. The process in accordance with claim 93  
2    wherein said diblock and triblock copolymers have a molecular  
3    weight between 2,000 D and 700 kD.

1           Claim 118. The process in accordance with claim 93  
2    wherein said diblock and triblock copolymers self-assemble in  
3    polymeric micelles in aqueous solution.

1           Claim 119. The process in accordance with claim 93  
2    wherein said diblock and triblock copolymers self-assemble in  
3    stabilized nanoparticles in aqueous solution.

1           Claim 120. The diblock copolymer prepared by the process  
2    of claim 93.

1           Claim 121. The diblock copolymer of claim 120 wherein  
2    said diblock copolymer is poly(N-vinylpyrrolidone)-*block*-poly  
3    (D, L -lactide).



1           Claim 122. The triblock copolymer prepared by the  
2    process of claim 93.

1           Claim 123. The triblock copolymer of claim 122 wherein  
2    said triblock copolymer is poly(D,L-lactide)-*block*-poly (N-  
3    vinylpyrrolidone)-*block*-poly (D, L-lactide).